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Survivability, Structures, and Materials Directorate Technical Report

Crevice Corrosion Performance of Candidate Naval Ship Seawater Valve Materials in Quiescent and Flowing Natural Seawater

by

D.M. Aylor, R.A. Hays, and R.J. Ferrara



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LIST OF ABBREVIATIONS

% Percent

Al Aluminum

BHN Brinell Hardness Number

°C Degrees Celsius

Cb Columbium cm Centimeter

Co Cobalt

CP Ti Commercially Pure Titanium

Cr Chromium

Cu Copper

Cu-Ni Copper-Nickel

°F Degrees Fahrenheit

Fe Iron

ft-lb Foot-pound

ft/sec Feet per second

gal/min Gallons per minute

HRB Hardness Rockwell B

HRC Hardness Rockwell C

ID Inner diameter

in. Inch

in-lb Inch-pound

kg-m Kilogram-meter

I/min Liters per minute

max Maximum
mg Milligram
min Minimum

mm Millimeter
Mn Manganese

MPa Megapascal

m/sec Meters per second

N Nitrogen

Nb

Niobium

Ni

Nickel

Ni Al Bronze

Nickel Aluminum Bronze

Ni-Cu

Nickel-copper

N-m

Newton-meter

0

Oxygen

OD

Outer diameter

Pb

Lead

psi

Pounds per square inch

PTFE

Polytetrafluoroethylene

Sn

Tin

Ta

Tantalum

Ti

Titanium

Ti-6Al-4V

Titanium-6Aluminum-4Vanadium

Ti-45Nb

Titanium-45Niobium

μin

Microinch

μm

Micron

W

Tungsten

Zn

Zinc

ABSTRACT

A wide range of alloys is being evaluated for use in a new generation of seawater valves for the U.S. Navy. This new generation of valves is being developed to reduce valve life cycle costs and to ensure materials compatibility with advanced seawater piping materials such as commercially pure titanium. Part of the evaluation includes assessing the corrosion performance of candidate valve materials. Crevice corrosion performance is of particular interest since valves are connected to shipboard piping systems with flanges and since valves contain numerous internal crevices.

Crevice corrosion tests were performed in constant temperature, natural seawater under both quiescent and flowing conditions. Bronze, copper-nickel, and nickel-copper alloys, which are currently used in Navy valves, were used as standards by which the performance of stainless steel, nickel-base, titanium, and cobalt alloys could be measured. No crevice corrosion was observed on any of the titanium or cobalt alloys tested while the stainless steel and nickel-base alloys ranged from fully resistant to highly susceptible. Wrought alloys were typically more resistant to crevice corrosion than their cast equivalents.

ADMINISTRATIVE INFORMATION

This work was performed under the Future Naval Capabilities Option sponsored by the Office of Naval Research (ONR). The technical points of contact at ONR during the course of this work have been CMDR Michael Kiley, Dr. A. John Sedriks, and Mr. David Thurston. The work was performed in the Marine Corrosion Branch (Code 613) of the Naval Surface Warfare Center, Carderock Division (NSWCCD). Funding for the program was managed under work unit numbers 1-6130-383 and 1-6130-394. Supervision was provided by Mr. Robert Ferrara, NSWCCD Code 613.

INTRODUCTION

Seawater piping systems and their associated components (pumps, valves, etc.) on Navy surface ships suffer from relatively high failure rates in service. The costs associated with seawater valves alone have been identified as a significant driver in the

overall maintenance budgets of Navy surface ships. To reduce seawater valve life cycle costs, passive film forming alloys are being considered as alternatives to current valve materials (typically bronze and nickel-copper alloy 400). These passive film-forming materials have increased corrosion resistance to most forms of corrosion as well as galvanic compatibility with titanium. However, these alloys may also be susceptible to crevice corrosion. In order to assist in the selection of materials for new valves, a broad range of alloys was evaluated in crevice corrosion tests in quiescent and flowing natural seawater. Results of these tests are reported herein.

MATERIALS

Both wrought and cast alloys were evaluated for seawater crevice corrosion resistance. Nominal compositions and mechanical properties of the alloys tested are found in Tables 1-3. Materials currently used in Navy seawater valves, both as body materials and as internal components (stem and trim) were used as controls in the tests. These materials include bronze, copper-nickel (Cu-Ni), and nickel-copper (Ni-Cu) alloys. In addition, stainless steels (austenitic, superaustenitic, and duplex), titanium alloys, cobalt alloys, and nickel alloys (nickel-chromium-molybdenum (Ni-Cr-Mo)) were evaluated. With the exception of the cast Alloy 59, which was obtained as a keel block, all castings were obtained in the form of ½ in. (6.35 mm) thick investment castings.

Table 1. Nominal Compositions and Mechanical Properties of Bronze, Copper-Nickel, and Nickel-Copper Alloys

					Mechanical Properties	roperties	
Alloy		Nominal		Tensile	0.2% Yield	Elongation,	
Designation	UNS Number	Composition	Condition	Strength, ksi ⁽¹⁾	Strength, ksi ⁽¹⁾ Strength, ksi ⁽¹⁾	% in 2-in.	Hardness
M Bronze	C92200	Cu-6Sn-2Pb-4Zn	As-Cast	34	16	24	
Ni Al Bronze	C95800	Cu-9Al-4.5Ni-4Fe	As-Cast or Temper Annealed	85	35	15	
90/10 Cu-Ni	C70600	Cu-10Ni	Annealed Bar	38 min	15 min	30 min	
Alloy 400	N04400	63Ni-28Cu-2Fe-2Mn	Hot Finished Bar	80-110	40-100	06-09	75-100 HRB
Cast M35	N24135	63Ni-28Cu-2Fe-2Mn	As-Cast	65 min	30 min	25 min	
Alloy K-500	N05500	Ni-30Cu-3Al-2Fe	Hot Finished and Age Hardened	140	100	20	27 HRC
70/30 Cu-Ni	C71500	Cu-30Ni	1-in. Hot Rolled Plate	55	20	45	35 HRB
70/30 Cu-Ni	C96400	Cu-30Ni	As-Cast	68	37	28	
3							

 $^{(1)}$ 1 ksi = 6.895 MPa

Table 2. Nominal Compositions and Mechanical Properties of Stainless Steels and Titanium Alloys

					Mechanical Properties	operties	
Alloy		Nominal		Tensile	0.2% Yield	Elongation,	
Designation	UNS Number	Composition	Condition	Strength, ksi ⁽¹⁾	Strength, ksi ⁽¹⁾ Strength, ksi ⁽¹⁾	% in 2-in.	Hardness
316L	S31603	Fe-18Cr-14Ni-3Mo-2Mn	Annealed	78	30	55	76 HRB
CF3M	192800	Fe-19Cr-10Ni-3Mo-2Mn	As-Cast	70 min	30 min	30 min	
CN7M	V08007	Fe-20Cr-29Ni-4Cu-3Mo	As-Cast	62	25	35	
AL6XN	29E80N	Fe-24Ni-21Cr-6Mo		108	. 53	47	88 HRB
CN3MN	J94651	Fe-24Ni-21Cr-6Mo	As-Cast	80 min	38 min	35 min	
254 SMO	S31254	Fe-18Ni-20Cr-6Mo	Annealed	94 min	44 min	35 min	
CK3MC _u N	J93254	Fe-18Ni-20Cr-6Mo	As-Cast	80 min	38 min	35 min	
654 SMO	S32654	Fe-22Ni-24Cr-7Mo-3Mn	Annealed	109 min	62 min	40 min	
Alloy 2507	S39275	Fe-25Cr-7Ni-4Mo-0.2N		116 min	80 min	25 min.	28 HRC max
Zeron 100	S32760	Fe-25Cr-7Ni-3.5Mo-0.2N		109 min	80 min	25 min	28 HRC max
SCF 23	S21000	Fe-23Cr-18Ni-5.5Mo- 4Mn-0.4N	Annealed	120	63	52	
Ti-6Al-4V, Gr. 5	R56400	Ti-6Al-4V	Mill Annealed	130 min	120 min	10 min	36 HRC
CP Titanium, Gr. 2	R50400	Ti-0.3Fe(max)- 0.25O(max)	Mill Annealed	50	40	20	
Ti-45Nb	R58450	Ti-45Nb	Wrought Product	79.2	69.6	23 (1")	

 $^{^{(1)}}$ 1 ksi = 6.895 MPa

Table 3. Nominal Compositions and Mechanical Properties of Nickel and Cobalt Alloys

					Mechanical Properties	perties	
Alloy		Nominal		Tensile	0.2% Yield	Elongation,	
Designation	UNS Number	Composition	Condition	Strength, ksi ⁽¹⁾	Strength, ksi ⁽¹⁾ Strength, ksi ⁽¹⁾	% in 2-in.	Hardness
Alloy 625	N06625	Ni-21Cr-8Mo-4Fe-3Nb	Annealed Bar, <4 in.	120	09	30	150-220 BHN
CW6MC	N26625	60Ni-21Cr-9Mo	As-Cast	20	40	20	
Alloy C-276	N10276	Ni-15Cr-16Mo-4W- 5Fe-2Co	Solution Treated Plate, 1 in.	113.9	52.9	59	
CW12MW	N30002	Ni-17Mo-16Cr-4W- 6Fe	As-Cast	72	40	4	
Alloy C22	N06022	Ni-20.5Cr-14Mo-3W- 2Fe-3Co	Solution Treated Bar, 0.5-2 in.	111	52	70	
CX2MW	N26022	Ni-21Cr-13.5Mo-3W- 4Fe	As-Cast	80	45	30	
Alloy 686	N06686	Ni-21Cr-16Mo-4W- 5Fe	Annealed Plate, 0.5 in.	104.7	52.8	71	
Alloy 59	N06059	Ni-23Cr-16Mo-1Fe	Solution Treated Plate, 0.2-1.2 in.	103 min	50 min	45	
Alloy 59		Ni-23Cr-16Mo-1Fe	As-Cast	81.8	48.7	62.8	
Alloy C-2000	N06200	Ni-23Cr-16Mo-2Cu	Annealed Plate, 0.5 in.	110	50	89	
Alloy 625 Plus	N07716	Ni-20Cr-8Mo-7Fe-3Nb	Solution Treated and Aged	165 min	120 min	20 min	
Alloy 718	N07718	Ni-20Cr-3Mo-5Cb+Ta	Solution Treated and Aged	185 min	150 min	12	331 BHN
Alloy 925	N09925	Ni-22Fe-20Cr-3Mo- 2Ti-2Cu	Annealed and Aged	165	110	27	31 HRC
Haynes 25	R30605	10Ni-51Co-20Cr-15W- 3Fe	Hot Rolled and Solution Annealed Bar	147	73	09	22 HRC
Ultimet	R31233	Co-26Cr-9Ni-5Mo- 2W-3Fe	Mill Annealed Plate	147.8	79.3	36	30 HRC
(1) 4 Los = 6 OOF MDC	JE NO.						

 $^{(1)}$ 1 ksi = 6.895 MPa

EXPERIMENTAL PROCEDURE

Quiescent Seawater Testing

Crevice corrosion specimen assemblies were immersed in constant temperature 85 ± 5 °F (29 ± 3 °C), quiescent, filtered natural seawater for a period of 180 days. The specimen assemblies consisted of two non-metallic disks attached to a 4 in. x 6 in. x nominally ¼ in. thick (10.2 cm x 15.2 cm x 0.6 cm) plate of the alloy being investigated, with crevices formed either by 1/8-in. (0.3 cm) thick gasket material (cloth inserted rubber per HH-P-151) or polytetrafluoroethylene (PTFE) with a specific gravity of 2.15 (Figures 1 and 2). Generally, rubber gasket material was used to form crevices on cast materials anticipated for valve bodies. This configuration replicated flange connections or valve bonnet connections. PTFE was generally used to form crevices on wrought materials. This configuration was intended to replicate crevices formed by "soft" seats on valve internal components.

Duplicate crevice assemblies were tested for each alloy. Each specimen was prepared with either a smooth (surface ground to 20 to 59 μ in (0.5 to 1.5 μ m)) or phonographic (500 to 1000 μ in (12.7 to 25.4 μ m), 30 to 80 serrations of uniform depth per inch of face width) surface finish within the area shown in Figure 1. All of the alloys were evaluated with smooth, surface ground finishes; phonographic finishes were additionally applied to specimens of M Bronze, 90/10 Cu-Ni, 70/30 Cu-Ni, Cast CF3M, and Cast CW6MC.

Prior to immersion in seawater, all specimens were degreased with acetone, brushed with a detergent-pumice mixture, water rinsed, and finally degreased with fresh acetone. For the anodized commercially pure titanium (CP Ti) specimens, the cleaning procedure was performed prior to anodizing; afterward, specimens were only acetone degreased. Anodizing was applied to the CP Ti specimens per AMS 2488C.

The crevice assemblies were tightened to a torque level of 75 in-lbs (0.42 N-m) and immersed in seawater. Seawater was continuously provided to the test tanks during the test period at a rate of approximately 0.2 to 0.3 gal./min. (0.75 to 1.13 l/min.), equating to about 3.5 complete changes of seawater daily. Copper-based alloys were tested in a tank separated from other alloys (Alloy 400 was tested with the copper-base alloys). After testing, corroded specimens were acid cleaned in accordance with ASTM

G1 to remove adhered corrosion products. Resistant specimens were scrubbed with a detergent brush to remove accumulated biofilms. Susceptibility to crevice corrosion was characterized in terms of the number of initiated sites and maximum depth of attack. The depth of attack measurements were made using a needlepoint dial depth gauge.

Flowing Seawater Testing

In these tests, seawater was pumped through a series of cells consisting of 4-6 plate specimens containing a 2-in. (5.1 cm) diameter hole sandwiched between nonmetallic crevice formers and flanged titanium spool pieces (Figures 3 and 4). Cells were assembled by placing the plate specimens over a centering device and applying a 200 psi (1.38 MPa) preload to the flange faces using a hydraulic press. The flange bolts were then torqued to 25 ft-lb (3.46 kg-m). This procedure was used in an attempt to produce consistent crevice tightness while also ensuring leak tight connections. The specimens were electrically isolated from the titanium spool pieces. Each specimen was 4 in. x 4 in. x nominally 1/4 in. thick (10.2 cm x 10.2 cm x 0.6 cm) and contained a 2 in. (5.1 cm) diameter center bore and a 3 in. (7.6 cm) outer diameter crevice area. Like the quiescent seawater tests, rubber gasket material was generally used as a crevice former on materials anticipated for use as valve bodies while PTFE was generally used to form crevices on alloys anticipated as trim materials. The surface ground and phonographic surface finishes used in the flowing seawater tests were the same as those used in the quiescent tests. Duplicate specimens per alloy condition were evaluated. All alloys in the quiescent seawater tests except CP Ti, Ti-6Al-4V, and 90/10 Cu-Ni were included in these flowing seawater tests. Specimens were exposed to filtered, natural seawater maintained at a constant 85 ± 5 °F (29 ± 3 °C) temperature and flowing at a velocity of 6 ft/sec (1.8 m/sec) for a period of 180 days. Prior to testing, all specimens and titanium components were detergent/pumice scrubbed with a bristle brush, then water rinsed and degreased with acetone. Crevice corrosion resistance of the alloys in flowing seawater was assessed in terms of mass loss, number of initiated crevice sites, and maximum depth of attack.

RESULTS

Quiescent and flowing seawater crevice corrosion results are provided in Tables 4-9. For each alloy class, results are reported in terms of the number of initiated sites and the maximum depth of attack for duplicate specimens. For the alloys that showed susceptibility to crevice corrosion, the time to initiation (based on visual inspection) was rapid, affecting most materials within the first week of testing. The only exceptions to this were wrought alloys 625, 70/30 Cu-Ni, 718, and 625 Plus and cast alloys CX2MW, CW6MC, and 70/30 Cu-Ni, which initiated crevice attack within the first month of testing.

Quiescent Seawater Testing

Bronze, Copper-Nickel, and Nickel-Copper Alloys

Crevice corrosion results for these alloys are found in Table 4. All of the bronze, copper-nickel, and nickel-copper alloys exhibited crevice-related corrosion. In comparing the alloys based on the maximum depth of attack (Figure 5), the top performers in order from most-to-least resistant are wrought 70/30 Cu-Ni (surface ground), Cast 70/30 Cu-Ni (phonographic finish), M Bronze (phonographic finish), and M Bronze (surface ground).

Crevice attack of the M Bronze, Ni Al Bronze, and 90/10 Cu-Ni specimens was concentrated immediately adjacent to the crevice, which is common for copper alloys^{1,2} (Figure 6). Alloy 400, Alloy K500, and cast M35 all exhibited light corrosion within the crevice and more significant attack adjacent to the crevice former. For Alloys 400 and K500, gravity influenced the extent of crevice corrosion well beyond the crevice sites. These alloys also exhibited pitting on the boldly exposed surfaces (outside the machined area), with more numerous but smaller pits present on the Alloy 400 specimens than on Alloy K500. Pit depths ranged from 0.003 in. (0.07 to 0.08 mm) for Alloy 400 and 0.002 to 0.004 in. (0.04 to 0.09 mm) for Alloy K-500. Pitting of Alloy 400 and K500 in quiescent or low velocity seawater is typical². Cast M35 also experienced localized corrosion on the boldly exposed surfaces. Figure 7 includes representative photographs highlighting the variation in corrosion present on Alloy 400, Alloy K500, and cast M35. Wrought 70/30 Cu-Ni exhibited minimal corrosion both at and adjacent to the crevice mouth; a greater degree of crevice corrosion was found on the cast 70/30

Cu-Ni specimens as shown in Figure 8. For the three alloys where both surface ground and phonographic finishes were evaluated (M Bronze, cast 70/30 Cu-Ni, and 90/10 Cu-Ni), specimens with the phonographic finish exhibited slightly increased crevice corrosion resistance as compared to the corresponding surface ground specimens. Figure 9 highlights the difference in surface finish for the cast 70/30 Cu-Ni specimens.

Table 4. Quiescent Seawater Crevice Corrosion Results for Bronze, Copper-Nickel, and Nickel-Copper Alloys

				Sp	Specimen A	Sp	Specimen B
Alloy	Material	Crevice	Crevice	# of	Max. Depth of	# of	Max. Depth of
•	Condition	Former	Surface Finish	Initiated	Attack,	Initiated	Attack,
				Sites	in. (mm)	Sites	in. (mm)
	•			(max. 2)		(max. 2)	
M Bronze	Cast	Rubber	Surface Ground	-	0.004 (0.09)	1	0.021 (0.53)
		Gasket	Phonographic	_	0.013 (0.34)	_	0.013 (0.32)
Ni Al Bronze	Cast	Rubber	Surface Ground	2	0.024 (0.60)	2	<0.0004 (<0.01)
		Gasket					
M35	Cast	Rubber	Surface Ground	2	0.022 (0.57)	2	0.028 (0.71)
		Gasket					
Alloy K500	Wrought	PTFE	Surface Ground	2	0.050 (1.28)	2	0.047 (1.19)
Alloy 400	Wrought	PTFE	Surface Ground	2	0.026 (0.67)	2	0.027 (0.69)
70/30	Wrought	PTFE	Surface Ground	2	0.004 (0.10)	2	0.002 (0.04)
Ou-Ni							
70/30	Cast	Rubber	Surface Ground	2	0.007 (0.18)	2	0.021 (0.54)
Cn-Ni		Gasket	Phonographic	2	<0.0004 (<0.01)	2	0.010 (0.25)
90/10	Wrought	Rubber	Surface Ground	2	0.061 (1.54)	2	0.073 (1.86)
Cu-Ni		Gasket	Phonographic	2	0.041 (1.05)	2	0.050 (1.28)

Stainless Steels

Crevice corrosion results for the stainless alloys in quiescent seawater are provided in Table 5. Only one stainless alloy, superaustenitic 654 SMO, was fully resistant to crevice corrosion in the 180-day test. Another superaustenitic, SCF-23, ranked right below the 654 SMO in terms of maximum depth of attack (Figure 10). The SCF-23 specimens initiated crevice corrosion on only 2 of 4 crevice sites. The remaining stainless steels displayed significantly increased crevice corrosion. Although direct comparison is difficult due to the different crevice formers used in the tests, all of the cast alloys (rubber gasket crevice formers) had greater susceptibility than their wrought counterparts (PTFE crevice formers) based on maximum depth of attack (Figure 10). All crevice corrosion observed on stainless steels occurred under the crevice former. Figure 11 shows representative photographs of the varied attack present among the stainless steels tested, while Figure 12 exhibits the difference in crevice corrosion resistance between wrought AL6XN and its cast counterpart, CN3MN.

<u>Titanium Alloys</u>

The titanium alloy results are also found in Table 5. All of the titanium alloys were fully resistant to crevice corrosion. No evidence of crevice corrosion was found under the rubber gasket or PTFE crevice formers, nor was there any corrosion of the boldly exposed surfaces on the Ti-45Nb, Ti-6Al-4V, or CP Ti specimens with and without anodizing (Figure 13).

Table 5. Quiescent Seawater Crevice Corrosion Results for Stainless Steels and Titanium Alloys

				Spi	Specimen A	Spi	Specimen B
Alloy	Material Condition	Crevice Former	Crevice Surface Finish	# of Initiated Sites	Max. Depth of Attack	# of Initiated Sites	Max. Depth of Attack
				(max. 2)	in. (mm)	(max. 2)	in. (mm)
316L	Wrought	PTFE	Surface Ground	2	0.052 (1.33)	2	0.089 (2.27)
CN7M	Cast	Rubber Gasket	Surface Ground	2	0.156 (3.97)	2	0.076 (1.94)
CF3M	Cast	Rubber Gasket	Surface Ground	2	0.088 (2.23)	2	0.183 (4.66)
			Phonographic	2	0.098 (2.49)	2	0.148 (3.75)
AL6XN	Wrought	PTFE	Surface Ground	2	0.046 (1.17)	-	0.023 (0.59)
CN3MN	Cast	Rubber Gasket	Surface Ground	2	0.116 (2.94)	2	0.133 (3.39)
254 SMO	Wrought	PTFE	Surface Ground	2	0.030 (0.76)	2	0.068 (1.73)
CK3MCuN	Cast	Rubber Gasket	Surface Ground	2	0.130 (3.31)		0.066 (1.67)
654 SMO	Wrought	PTFE	Surface Ground	0	0	0	0
SCF 23	Wrought	PTFE	Surface Ground	_	0.134 (0.35)	_	0.023 (0.59)
Alloy 2507	Wrought	PTFE	Surface Ground	2	0.034 (0.87)	2	0.041 (1.04)
Zeron 100	Wrought	PTFE	Surface Ground	2	0.039 (0.98)	2	0.038 (0.97)
CP Titanium	Wrought	PTFE	Surface Ground	0	0	0	0
CP Titanium (anodized)	Wrought	PTFE	Surface Ground then Anodized	0	0	0	0
Ti-6Al-4V	Wrought	PTFE	Surface Ground	0	0	0	0
Ti-45Nb	Wrought	Rubber Gasket	Surface Ground	0	0	0	0

Nickel Alloys

Crevice corrosion data for the nickel alloys under quiescent conditions are found in Table 6. Numerous alloys in this series were fully resistant to crevice corrosion, including wrought alloys C22, 686, 59, and C2000 and cast Alloy 59. Three other nickel alloys exhibited an increased susceptibility in comparison with the fully resistant alloys but were markedly improved compared to the remaining cast nickel alloys tested (Figure 14). These materials are wrought Alloys C276 and 625, and Alloy 625 Plus. In all cases where both cast and wrought versions of the same alloy were tested, the wrought materials consistently performed better than the castings. Again, this result may have been influenced by the different crevice formers used for the wrought and cast alloys. Representative photographs of cast and wrought nickel-base alloys are found in Figures 15 and 16. Cast CW6MC, the only nickel alloy where both surface ground and phonographic finishes were evaluated, showed slightly improved resistance in the phonographic condition (Figure 17). Similar to the stainless steels, crevice corrosion of the nickel base alloys occurred under the crevice former.

Cobalt Alloys

The two cobalt alloys, Ultimet and Haynes 25, displayed full resistance to crevice corrosion in quiescent seawater (Table 6). No attack was observed under the PTFE crevice formers or on the boldly exposed surfaces of any of these specimens.

Table 6. Quiescent Seawater Crevice Corrosion Results for Nickel and Cobalt Alloys

				Sp	Specimen A	Spe	Specimen B
Allov	Material	Crevice	Crevice Surface	# of		# of	
•	Condition	Former	Finish	Initiated	Max. Depth of	Initiated	Max. Depth of
				Sites	Attack	Sites	Attack
				(max. 2)	in. (mm)	(max. 2)	in. (mm)
Alloy 625	Wrought	PTFE	Surface Ground	_	0.007 (0.18)	2	0.002 (0.04)
CW6MC	Cast	Rubber Gasket	Surface Ground	2	0.087 (2.21)	-	0.028 (0.70)
			Phonographic		0.021 (0.53)		0.065 (1.66)
Alloy C276	Wrought	PTFE	Surface Ground	-	0.004 (0.10)	_	0.005 (0.13)
CW12MW	Cast	Rubber Gasket	Surface Ground	_	0.111 (2.83)	2	0.106 (2.68)
Alloy C22	Wrought	PTFE	Surface Ground	0	0	0	0
CX2MW	Cast	Rubber Gasket	Surface Ground	0	0	_	0.039 (0.98)
Alloy 686	Wrought	PTFE	Surface Ground	0	0	0	0
Alloy 59	Wrought	PTFE	Surface Ground	0	0	0	0
Alloy 59	Cast	Rubber Gasket	Surface Ground	0	0	0	0
Alloy C2000	Wrought	PTFE	Surface Ground	0	0	0	0
Alloy 625 Plus	Wrought	PTFE	Surface Ground	2	0.017 (0.43)	2	0.015 (0.37)
Alloy 718	Wrought	PTFE	Surface Ground	2	0.046 (1.18)	-	0.018 (0.46)
Alloy 925	Wrought	PTFE	Surface Ground	2	0.103 (2.61)	2	0.125 (3.18)
Ultimet	Wrought	PTFE	Surface Ground	0	0	0	0
Haynes 25	Wrought	PTFE	Surface Ground	0	0	0	0

Flowing Seawater Testing

Bronze, Copper-Nickel, and Nickel-Copper Alloys

Crevice corrosion results for the bronze, copper-nickel, and nickel-copper alloys in flowing seawater conditions are found in Table 7. Specimen mass loss measurements are included with this data since corrosion was noted in areas other than within the crevice, including both the interior bore surfaces and on the boldly exposed surfaces outside the machined crevice area. Corrosion in the areas adjacent to the crevice was not unexpected since localized corrosion of copper alloys is typically present outside the crevice due to metal-ion concentration cell effects¹. Based on the mass loss measurements, the best performing alloys were the cast and wrought 70/30 Cu-Ni.

The M Bronze specimens did not exhibit corrosion under the rubber gasket crevice formers. However, one of the two specimens did display corrosion on the boldly exposed surfaces outside the machined area. The Ni Al Bronze specimens showed a slight degree of attack adjacent to the gasket but within the machined area, and corrosion on the boldly exposed surfaces adjacent to the machined area was also evident.

The extent of mass loss for the M Bronze specimens was significantly less than for the Ni Al Bronze. The majority of the attack on the Ni Al Bronze and M Bronze specimens was within the bore surfaces, which was expected on these copper alloys due to the close proximity of the crevice area and the fact that the bore surfaces are anodic to the crevice area. Like one of the M Bronze specimens, cast M35 exhibited corrosion on the boldly exposed surfaces outside the machined area and no corrosion under the rubber gasket (Figure 18). Cast M35 additionally exhibited substantial pitting of the bore surfaces. The excessive mass loss reported for M35 Specimen B was presumably due to a dead short between the specimen and the titanium piping that was suspected based on corrosion potential measurements after 6 weeks' exposure. The mass loss reported for M35 Specimen A was similar to the average mass loss on the Ni Al Bronze specimens. Figure 19 depicts the corrosion present on the interior bore surfaces of cast Ni Al Bronze and M35.

Crevice corrosion initiated under the PTFE at all four crevice sites on the wrought Alloy 400 specimens (Figure 18). Localized attack was also present on the Alloy 400 bore surfaces. The average mass loss for the cast and wrought 70/30 Cu-Ni specimens was similar, but the occurrence of localized corrosion differed. The wrought 70/30 Cu-Ni specimens exhibited attack under the crevice, while the cast specimens showed slight corrosion immediately adjacent to the crevice former.

Table 7. Flowing Seawater (6 ft/sec (1.8 m/sec)) Crevice Corrosion Results for Bronze, Copper-Nickel, and Nickel-Copper Alloys

	T						1	_
	Mass	(mg)	520	2200	26,570³	4	320	210
Specimen B	Max. Depth of Attack	in. (mm)	01	<0.0004 (<0.01) ²	0	0.011 (0.27)	0.004 (0.11)	<0.0004 (<0.01) ²
	# of Initiated Sites	(max. 2)	0	2	0	2	2	2
	Mass Loss	(mg)	450	1420	1600	4	320	470
Specimen A	Max. Depth of Attack	ın. (mm)	0	<0.0004 (<0.01) ²	0,	0.010 (0.25)	0.007 (0.17)	$0.002 (0.05)^2$
	# of Initiated Sites	(max. 2)	0	2	0	2	2	2
	Crevice Surface Finish		Phonographic	Phonographic	Phonographic	Surface Ground	Surface Ground	Phonographic
	Crevice Former		Rubber Gasket	Rubber Gasket	Rubber Gasket	PTFE	PTFE	Rubber Gasket
	Material Condition		Cast	Cast	Cast	Wrought	Wrought	Cast
	Alloy		M Bronze	Ni Al Bronze	M35	Alloy 400	70/30 Cu-Ni	70/30 Cu-Ni

¹No corrosion under gasket but attack evident on boldly exposed surfaces outside machined area (not measured).

²Measured attack immediately adjacent to gasket and within machined area. ³Excessive mass loss due to suspected dead short between M35 specimen and titanium piping.

⁴Mass loss measurements inadvertently omitted.

Stainless Steels

Crevice corrosion results for the stainless steels in flowing seawater conditions are provided in Table 8. Like the quiescent seawater data, these results show that wrought 654 SMO was the only stainless alloy that was fully resistant after the 180-day test. Except for cast CN3MN and wrought Zeron 100, the remaining stainless steels each initiated crevice corrosion at all four crevice sites. Only one crevice site initiated on CN3MN, yet the depth of attack was significant (0.025 in. (0.63 mm)). As in the case of quiescent seawater, the cast alloys had lower crevice corrosion resistance than their wrought equivalents. In comparing the maximum depth of attack data for the stainless alloys in quiescent and flowing seawater (Figure 10), it is apparent that flowing seawater was a significantly less severe environment than quiescent seawater (the exception was CF3M with the phonographic finish). This is presumably due to differences in the "crevice area ratio", i.e. the ratio between the boldly exposed surface area and the area shielded by the crevice former. In quiet seawater, the crevice area ratio was 7:1 while in flowing seawater, the crevice area ratio was 1:5. Representative photographs showing the range of crevice corrosion present on three stainless steels are found in Figure 20, while Figure 21 highlights the differences in crevice corrosion between wrought 254 SMO and its cast counterpart, CK3MCuN.

Titanium Alloys

Ti-45Nb was the only titanium alloy included in the flowing seawater testing (Table 8). As in the quiescent seawater tests, Ti-45Nb was fully resistant. There was no evidence of crevice corrosion at any of the four crevice sites or on the boldly exposed surfaces of these specimens. It should also be noted that no crevice corrosion was observed on the flanged faces of the CP Ti spool pieces used in the specimen assemblies.

Table 8. Flowing Seawater (6 ft/sec (1.8 m/sec)) Crevice Corrosion Results for Stainless Steels and Titanium Alloys

				Spe	Specimen A	Spe	Specimen B
Alloy	Material Condition	Crevice Former	Crevice Surface Finish	# of Initiated Sites (max. 2)	Max. Depth of Attack in. (mm)	# of Initiated Sites (max. 2)	Max. Depth of Attack in. (mm)
316L	Wrought	PTFE	Surface Ground	2	0.019 (0.48)	. 2	0.006 (0.15)
CN7M	Cast	Rubber Gasket	Phonographic	2	0.060 (1.53)	2	0.016 (0.40)
CF3M	Cast	Rubber Gasket	Phonographic	2	Perforated	2	0.156 (3.95)
AL6XN	Wrought	PTFE	Surface Ground	2	0.001 (0.03)	2	<0.0004 (<0.01)
CN3MN	Cast	Rubber Gasket	Phonographic	_	0.025 (0.63)	0	0
254 SMO	Wrought	PTFE	Surface Ground	2	0.0004 (0.01)	2	<0.0004 (<0.01)
CK3MCuN	Cast	Rubber Gasket	Phonographic	2	0.052 (1.32)	2	0.058 (1.47)
654 SMO	Wrought	PTFE	Surface Ground	0	0	0	0
SCF 23	Wrought	PTFE	Surface Ground	2	<0.0004 (<0.01)	2	0.005 (0.12)
Alloy 2507	Wrought	PTFE	Surface Ground	2	<0.0004 (<0.01)	2	<0.0004 (<0.01)
Zeron 100	Wrought	PTFE	Surface Ground	2	<0.0004 (<0.01)	_	<0.0004 (<0.01)
Ti-45Nb	Wrought	PTFE	Surface Ground	0	0	0	0

Nickel Alloys

Numerous nickel alloys remained fully resistant after 180 days in flowing seawater (Table 9). These include wrought Alloys C22, 686, C2000, and C276 and cast alloys 59 and CW12MW. In comparing this list to the fully resistant nickel alloys in quiescent seawater, three differences are noted. Wrought Alloy 59 displayed minimal crevice corrosion (<0.0004 in. (<0.01 mm)) at two sites in flowing seawater yet was fully resistant in quiescent conditions. Wrought Alloy C276 was fully resistant in flowing seawater, but exhibited crevice corrosion at 2 of 4 sites with a maximum depth of attack of 0.0051 in. (0.13 mm) in quiescent seawater. The most significant difference in performance was found for Cast CW12MW. In quiescent seawater, crevice corrosion was present on 3 out of 4 sites and penetrated to a maximum attack depth of 0.112 in. (2.83 mm), as shown in Table 6. This is in stark contrast to the flowing seawater results, which showed full crevice corrosion resistance on both CW12MW specimens. The surface condition of the specimens was different (surface ground in quiescent vs. phonographic in flowing), which could have affected the results but most likely the marked differences were attributable to either casting defects and/or chemical segregation. Metallographic analysis is required to delineate the reasons for the differing results.

The remaining nickel alloys all showed reduced resistance to crevice corrosion in flowing conditions. Wrought Alloy 625 exhibited minimal corrosion (<0.0004 in. (<0.01 mm)) at all four crevice sites, while cast CW6MC displayed corrosion with a maximum depth of attack of 0.0047 in. (0.12 mm) on one of two specimens. This crevice corrosion is suspect, however, because the specimen was found to be dead shorted to the titanium piping after 6 weeks' seawater exposure. Alloy 625 is known to be susceptible to crevice attack in seawater³, and it is unknown whether the coupling to titanium exacerbated the extent of corrosion in the present case. Wrought Alloy 625 Plus showed slightly increased crevice attack as compared to wrought Alloy 625, but Alloy 625 Plus ranked higher in resistance than Alloy 925. The most substantial crevice corrosion of the nickel alloys was found on Alloy 718. Crevice corrosion was found at 3 crevice sites and the maximum depth of

attack was 0.0248 in. (0.63 mm). Figure 22 includes representative photographs of the crevice specimens for wrought Alloys 718, 925, and C2000.

Very little difference was noted in the maximum depth of attack data for flowing seawater between cast and wrought versions of the same alloy. While the data show wrought Alloys C22 and 625 performed slightly better than their cast counterparts (CX2MW and CW6MC, respectively) the overall depths of attack are very low in all cases. The slight increase in susceptibility in the cast materials could also be a result of the use of the gasket crevice formers as opposed to the PTFE crevice formers used for the wrought alloys.

The maximum depth of attack data for the nickel alloys in flowing seawater showed significantly better crevice corrosion resistance than in quiescent seawater. As was stated for the stainless steels, this can be attributed to differences in the crevice area ratios for the quiescent and flowing tests.

Cobalt Alloys

The two cobalt alloys, Haynes 25 and Ultimet, were fully resistant to crevice corrosion in flowing conditions (Table 9 and Figure 23). There was no indication of corrosion present on any of these specimens.

Table 9. Flowing Seawater (6 ft/sec (1.8 m/sec)) Crevice Corrosion Results for Nickel and Cobalt Alloys

				Sp	Specimen A	Sp	Specimen B
				# of		# of	
			,	Initiated	Max. Depth of	Initiated	Max. Depth of
Allov	Material Condition	Crevice Former	Crevice Surface Finish	Sites (max. 2)	Attack in. (mm)	Sites (max. 2)	Attack in. (mm)
Alloy 625	Wrought	PTFE	Surface Ground	2	<0.0004 (<0.01)	2	<0.0004 (<0.01)
CW6MC	Cast	Rubber Gasket	Phonographic	21	0.005 (0.12)	0	0
Alloy C276	Wrought	PTFE	Surface Ground	0	0	0	0
CW12MW	Cast	Rubber Gasket	Phonographic	0	0	0	0
Alloy C22	Wrought	PTFE	Surface Ground	0	0	0	0
CX2MW	Cast	Rubber Gasket	Phonographic	•	0.002 (0.04)	_	0.005 (0.12)
Alloy 686	Wrought	PTFE	Surface Ground	0	0	0	0
Alloy 59	Wrought	PTFE	Surface Ground	-	<0.0004 (<0.01)	_	<0.0004 (<0.01)
Alloy 59	Cast	Rubber Gasket	Phonographic	0	0	0	0
Alloy C2000	Wrought	PTFE	Surface Ground	0	0	0	0
Alloy 625 Plus	Wrought	PTFE	Surface Ground	_	<0.0004 (<0.01)	_	0.001 (0.02)
Alloy 718	Wrought	PTFE	Surface Ground	2	0.003 (0.08)	-	0.025 (0.63)
Alloy 925	Wrought	PTFE	Surface Ground	2	0.002 (0.04)	2	0.002 (0.04)
Ultimet	Wrought	PTFE	Surface Ground	0	0	0	0
Haynes 25	Wrought	PTFE	Surface Ground	0	0	0	0
				•			

¹These results are suspect since this specimen was found to be shorted to the Ti piping after 6 weeks.

Summary of Quiescent and Flowing Seawater Results

Bronze, Nickel-Copper, and Copper-Nickel Alloys

All of the alloys in this group exhibited crevice corrosion in both quiescent and flowing conditions. The localized attack was concentrated at the mouth of the crevice formers due to metal-ion concentration effects. Additionally, some of the alloys exhibited localized corrosion under the crevice former. These alloys include cast 70/30 Cu-Ni, M35, and alloy K500 (quiescent seawater), wrought 70/30 Cu-Ni (flowing seawater) and alloy 400 (quiescent and flowing seawater). An evaluation of surface finish (surface ground vs. phonographic) for M Bronze, cast 70/30 Cu-Ni, and 90/10 Cu-Ni in quiescent seawater identified slightly increased crevice corrosion resistance for the phonographic finish specimens.

Stainless Steels

Only one stainless alloy, superaustenitic 654 SMO, remained fully resistant in both quiescent and flowing seawater after 180 days. Where both wrought and cast versions of the same alloy were tested (254 SMO and CK3MCuN, AL6XN and CN3MN, 316L and CF3M), the wrought alloys exhibited improved crevice corrosion resistance over the cast products. This result may have been influenced by the different crevice formers used to test the cast and wrought materials. The more compliant rubber gasket material used for the cast materials can maintain a tighter crevice as corrosion propagates than the PTFE material used for the wrought alloys. However, as recently demonstrated for CF3M in other gasketed crevice tests, PTFE promoted more attack than various rubber-type gaskets when applied to ground flange surfaces⁴. Cast CF3M, evaluated in both surface ground and phonographic conditions, showed slightly improved crevice resistance for the phonographic specimens in quiescent seawater. Also, the crevice corrosion resistance of the alloys in the flowing seawater test was significantly improved over that observed under quiescent conditions. This was presumably due to differences in the crevice geometry and in crevice area ratios for the specimens rather than an environmental effect.

Titanium Alloys

Wrought Ti-45Nb was fully resistant in the quiescent and flowing seawater testing. CP Ti (with and without anodizing) showed full resistance in quiescent seawater. Although CP Ti was not tested as a "specimen" under flowing conditions, no crevice corrosion was observed on any of the 22 CP Ti flanges used to make up the specimen assemblies. Crevices were formed on the flange specimens by both rubber gaskets and PTFE annuli depending on the particular specimen assembly. Ti-6Al-4V was fully resistant to crevice corrosion under quiescent conditions.

Nickel Alloys

Four nickel alloys exhibited full resistance to crevice corrosion in both quiescent and flowing seawater. These materials include wrought Alloys C22, 686, and C2000, and cast Alloy 59. Wrought Alloy 59 exhibited full resistance in quiescent seawater and had less than 0.0004 in. (0.01 mm) depth of attack at 2 of 4 sites in flowing conditions. Wrought and cast versions of nickel alloys in quiescent and flowing seawater generally showed increased crevice corrosion resistance for the wrought alloy as compared to the casting. Two exceptions, wrought 59/cast 59 (quiescent and flowing seawater) and wrought C276/cast CW12MW (flowing seawater), showed no substantial difference in resistance between the wrought and cast materials. Cast CW6MC crevice specimens containing a phonographic finish exhibited slightly increased crevice resistance as compared to the CW6MC surface ground specimens in quiescent seawater.

Cobalt Alloys

Both Alloy 25 and Ultimet showed full resistance to crevice corrosion in both quiescent and flowing seawater.

CONCLUSIONS

Based on crevice corrosion tests in $85 \pm 5^{\circ}$ F ($29 \pm 3^{\circ}$ C) natural seawater and in freely corroding conditions, the following are concluded:

M Bronze, Ni Al Bronze, M35, Alloy 400, Alloy K500, 70/30 Cu-Ni, and 90/10 Cu-Ni
all exhibited susceptibility to crevice corrosion based on 180-day testing in quiescent
and/or flowing seawater. The crevice corrosion was concentrated outside the

- crevice, although some of these alloys additionally contained corrosion under the crevice formers.
- Numerous alloys were fully resistant to crevice corrosion in both quiescent and flowing seawater, including 654 SMO, Alloy C22, Alloy 686, Cast Alloy 59, Alloy C2000, Ti-45Nb, Ultimet, and Alloy 25. Wrought Alloy 59 was fully resistant in quiescent seawater and exhibited minimal crevice corrosion (<0.0004 in. (<0.01 mm)) in flowing seawater.
- Ti-6Al-4V and commercially pure titanium Grade 2 (with and without anodizing) were fully resistant to crevice corrosion in quiescent seawater conditions. These alloys were not tested in flowing seawater.
- A phonographic surface finish representative of that used on valve gasketed flange faces (500 to 1000 μin (12.7 to 25.4 μm)) resulted in a slight improvement in quiescent seawater crevice corrosion resistance as compared to a surface ground finish (20 to 60 μin (0.5 to 1.5 μm)).
- Generally, wrought alloys performed better than their cast counterparts in both
 quiescent and flowing seawater conditions. This result may have been influenced by
 the different crevice formers used to test the wrought and cast alloys (PTFE and
 rubber gaskets, respectively) or the differences may be due to defects and/or
 chemical segregation in the as-cast structures.
- Crevice corrosion resistance of alloys in flowing conditions was improved as
 compared to quiescent conditions. This is thought to be a result of differences in the
 crevice geometry and in the "crevice area ratio", i.e. the ratio between the boldly
 exposed surface area and the area shielded by the crevice former, rather than
 environmental effects. For the tests summarized herein, the crevice area ratio was
 7:1 for the quiescent exposures and 1:5 for the flowing exposures.

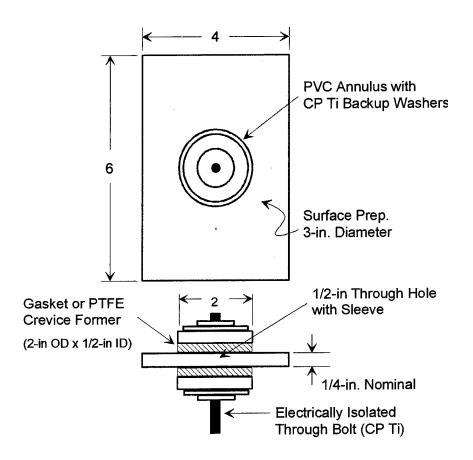


Figure 1. Crevice Corrosion Specimen Assembly Used for Quiescent Exposures

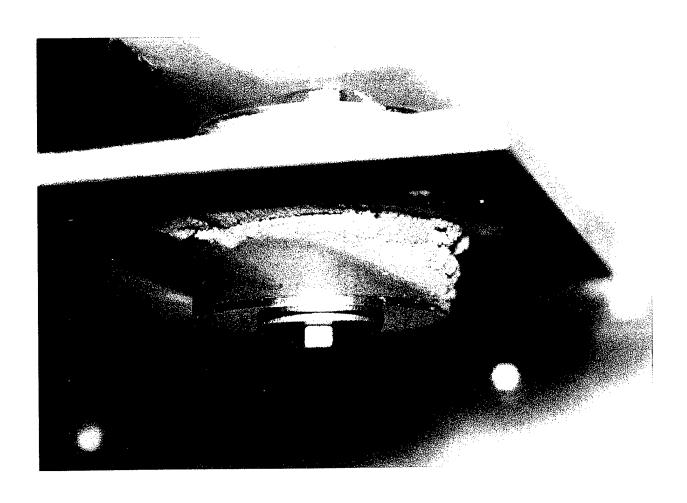


Figure 2. Representative Photograph of Specimen Assembly in Test (Quiescent Exposure)

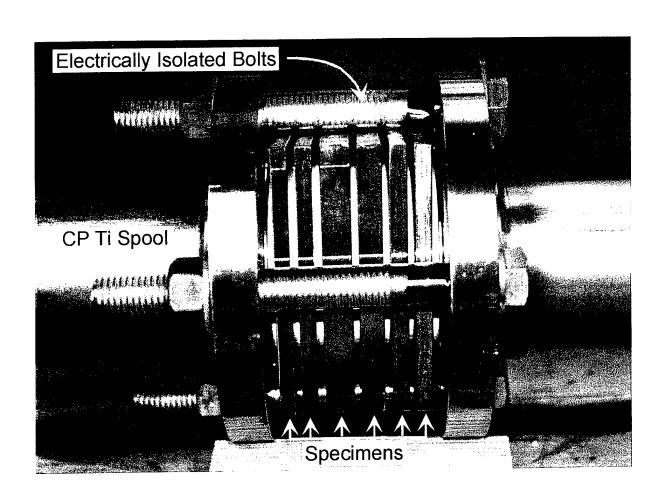


Figure 3. Specimen Assembly for Crevice Corrosion Tests in Flowing Seawater

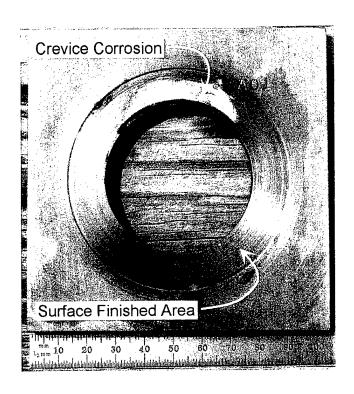


Figure 4. Crevice Corrosion Test Specimen (Flowing Seawater)

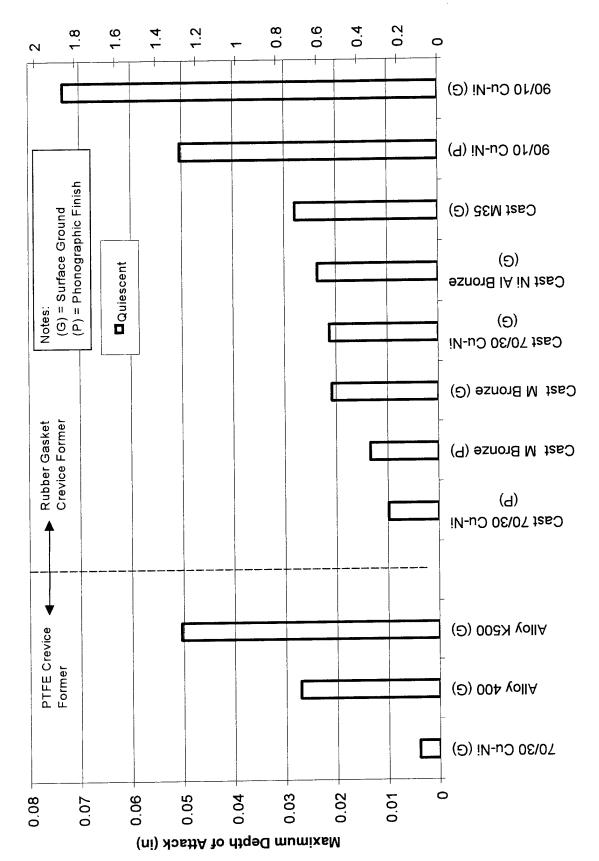


Figure 5. Maximum Depth of Attack Data for Bronze, Copper-Nickel and Nickel-Copper Corrosion Specimens After 180 Days in Quiescent Natural Seawater

30

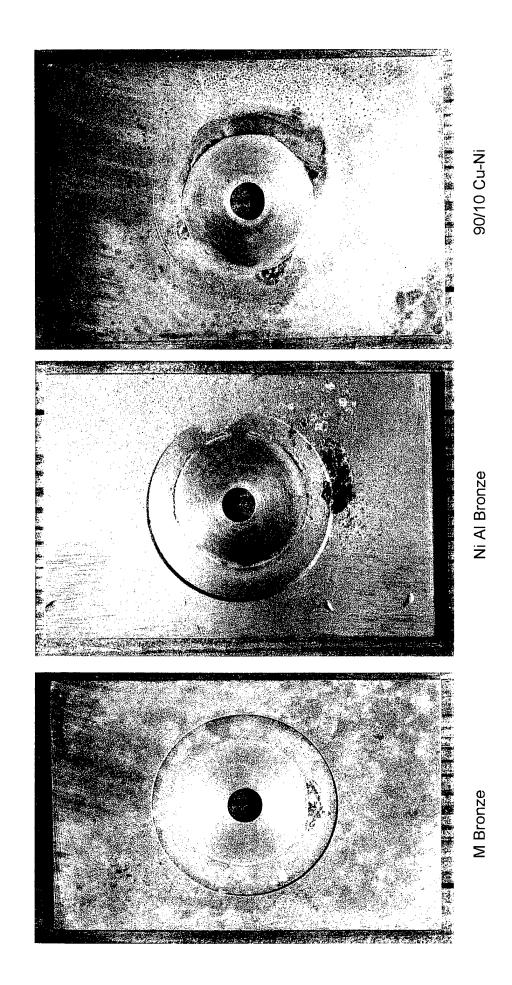


Figure 6. Cast M Bronze, Cast Ni Al Bronze, and Wrought 90/10 Cu-Ni Crevice Specimens After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater

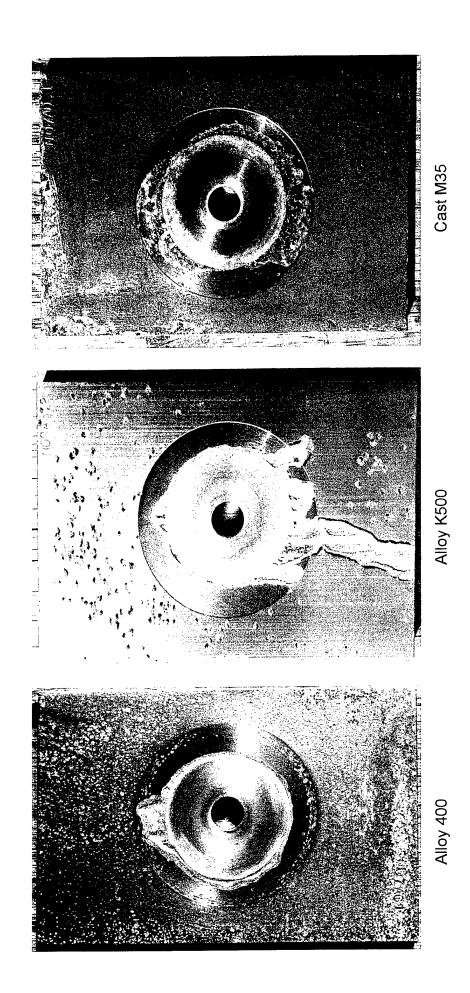
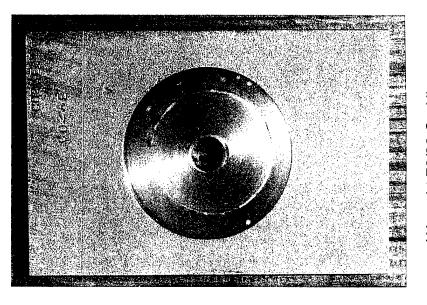
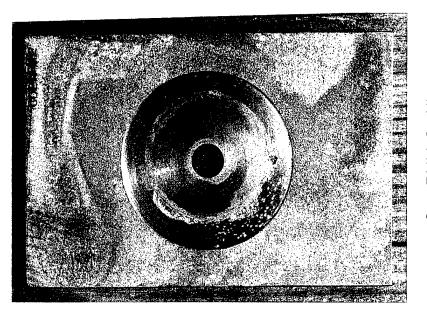


Figure 7. Wrought Alloy 400, Wrought Alloy K500, and Cast M35 Crevice Specimens After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater

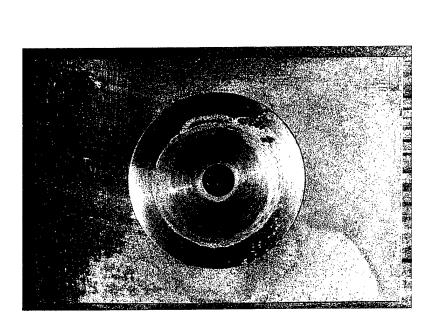


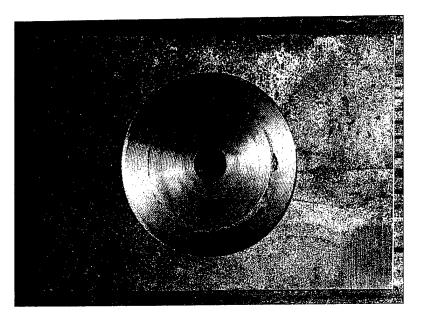
Wrought 70/30 Cu-Ni



Cast 70/30 Cu-Ni

Figure 8. Representative Condition of Wrought and Cast 70/30 Cu-Ni Crevice Specimens After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater





Phonographic Finish

Surface Ground

Figure 9. Cast 70/30 Cu-Ni Crevice Specimens with Surface Ground and Phonograph Finishes After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater

Maximum Depth of Attack (mm)

Figure 10. Maximum Depth of Attack Data for Stainless Steel Alloys After 180 Days in Quiescent and Flowing Natural Seawater

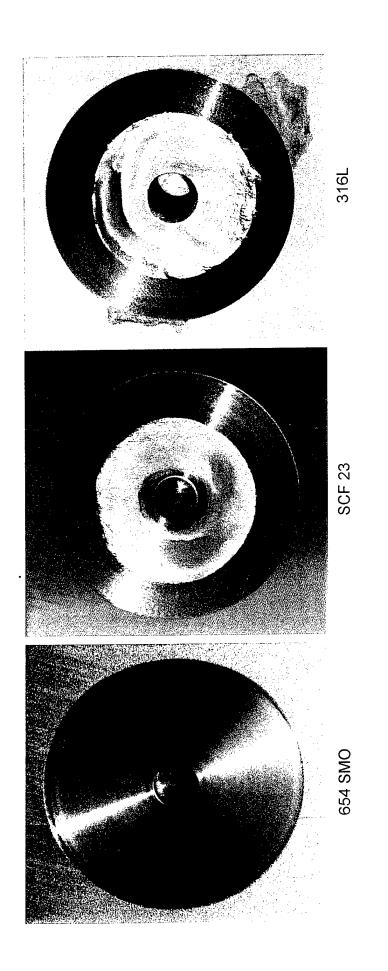
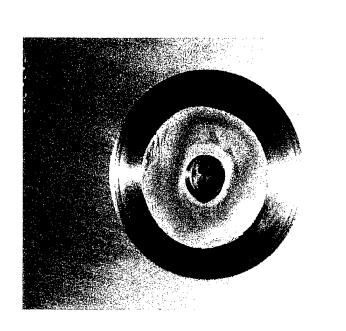
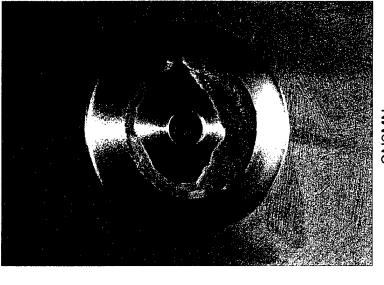


Figure 11. Wrought Stainless Steel Alloys After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater





CN3MN

ALGXN

Figure 12. Wrought AL6XN and Cast CN3MN Crevice Specimens After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater

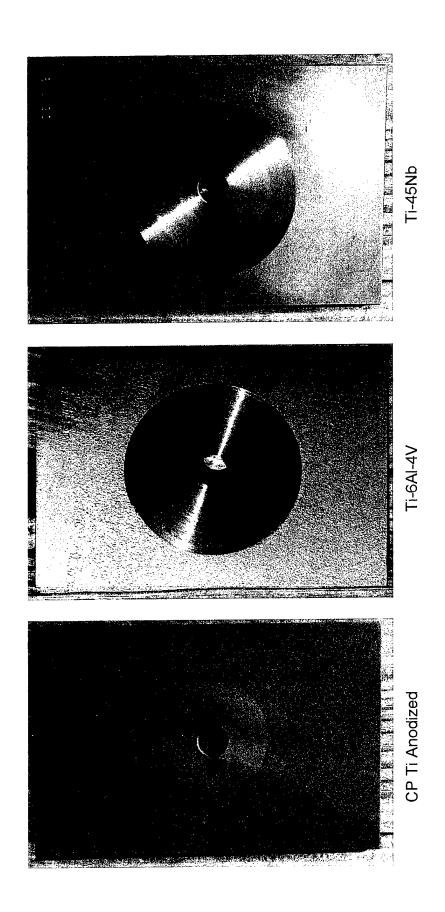


Figure 13. Titanium Alloys After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater



39

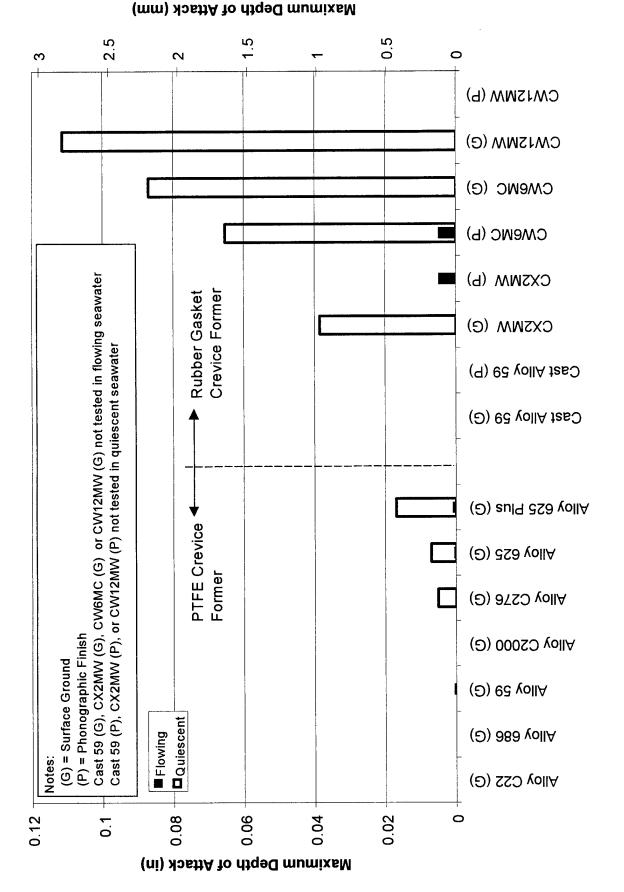


Figure 14. Maximum Depth of Attack Data for Nickel-Base Alloys After 180 Days in Quiescent and Flowing Natural Seawater

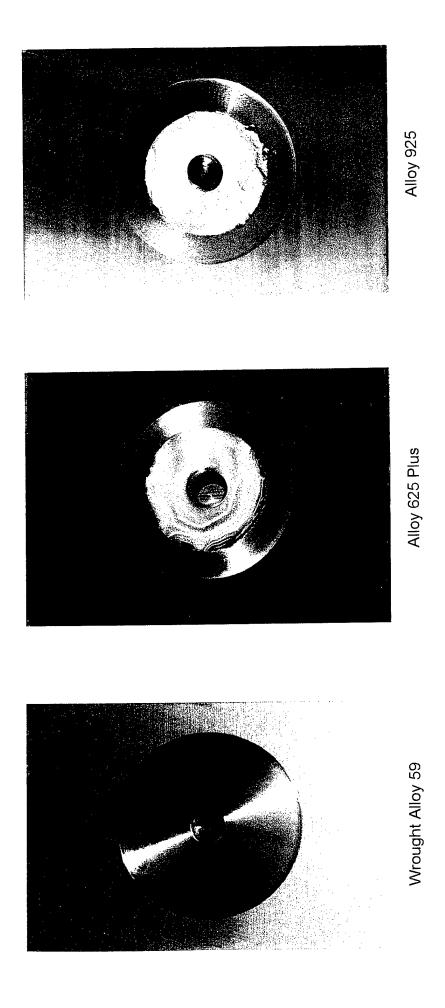
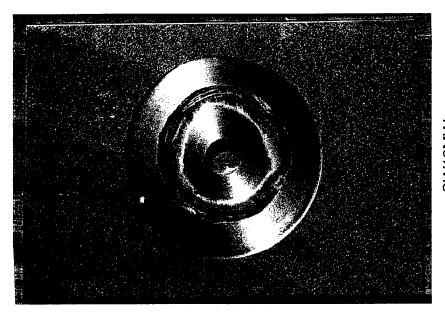


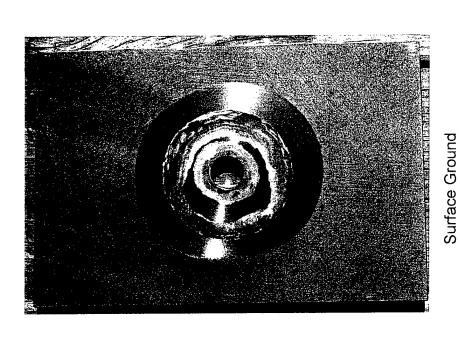
Figure 15. Representative Nickel-Base Alloy Crevice Specimens After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater

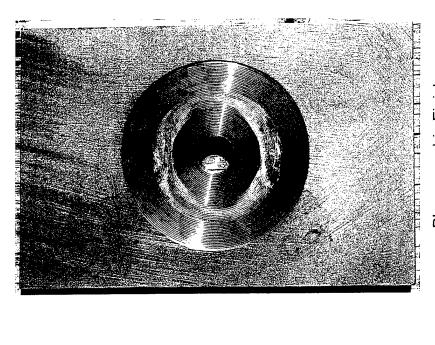




CW12MW

Figure 16. Wrought C276 and Cast CW12MW Crevice Specimens After 180 Days in 85 $\pm~$ 5°F (29 $\pm~$ 3°C) Quiescent, Natural Seawater





Phonographic Finish

Figure 17. Cast CW6MC Crevice Specimens with Surface Ground and Phonographic Finishes After 180 Days in 85 \pm 5°F (29 \pm 3°C) Quiescent, Natural Seawater

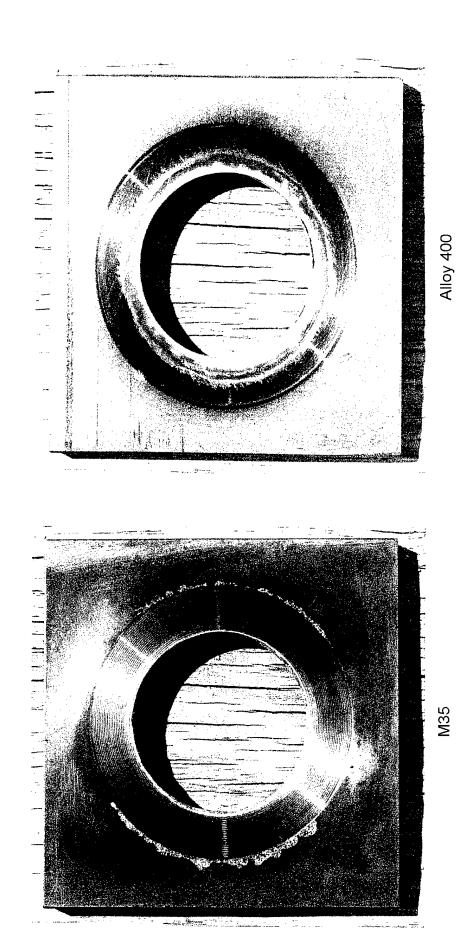
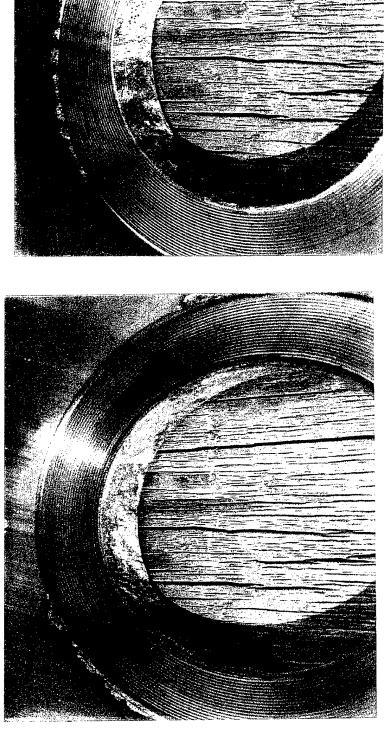
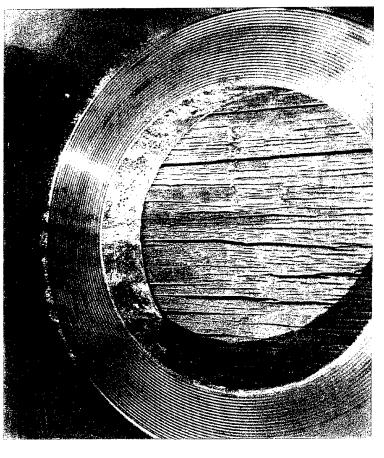


Figure 18. Cast M35 and Wrought Alloy 400 After 180 Days in 6 ft/sec (1.8 m/sec) Flowing Natural Seawater





M35 Specimen A

Ni Al Bronze

Figure 19. Interior Bore Surfaces of Cast Ni Al Bronze and M35 After 180 Days in 6 ft/sec (1.8 m/sec) Flowing Natural Seawater

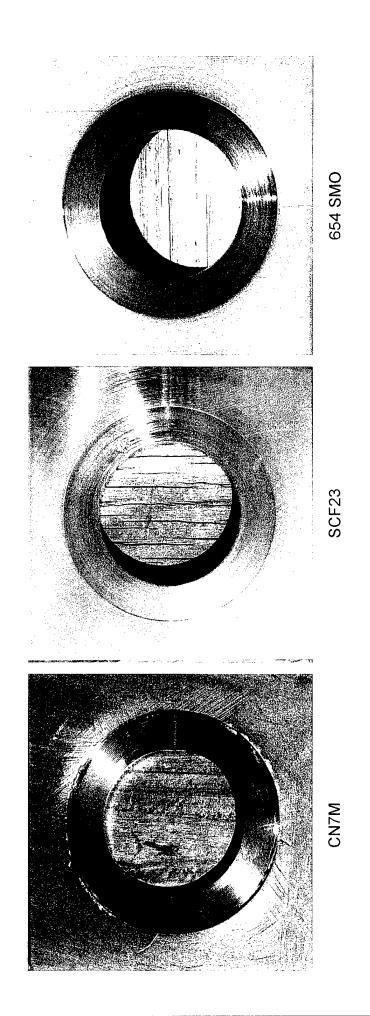
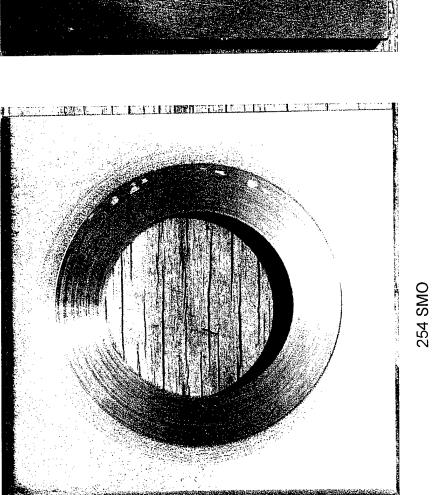
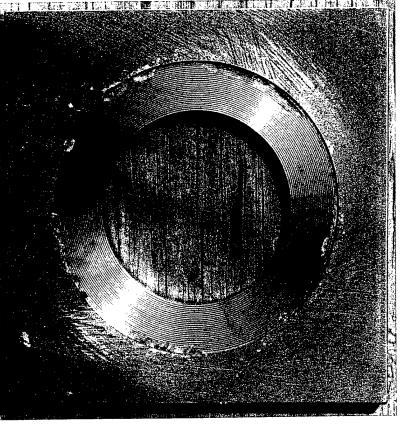


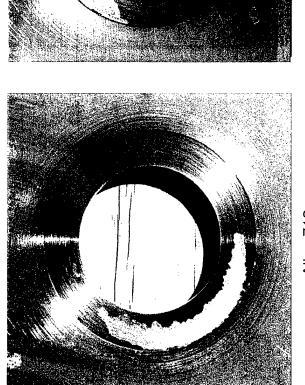
Figure 20. CN7M, SCF23, and 654 SMO After 180 Days in 6 ft/sec (1.8 m/sec) Flowing Natural Seawater

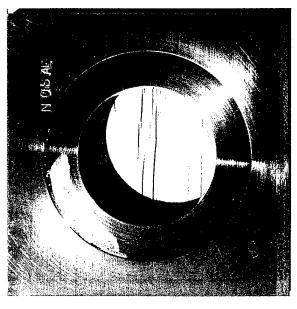


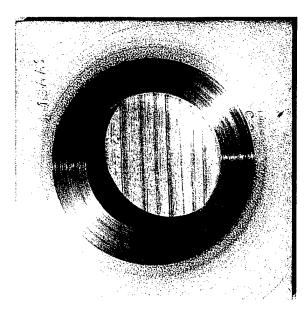


CK3MCuN

Figure 21. Wrought 254SMO and Cast CK3MCuN After 180 Days in 6 ft/sec (1.8 m/sec) Flowing Natural Seawater





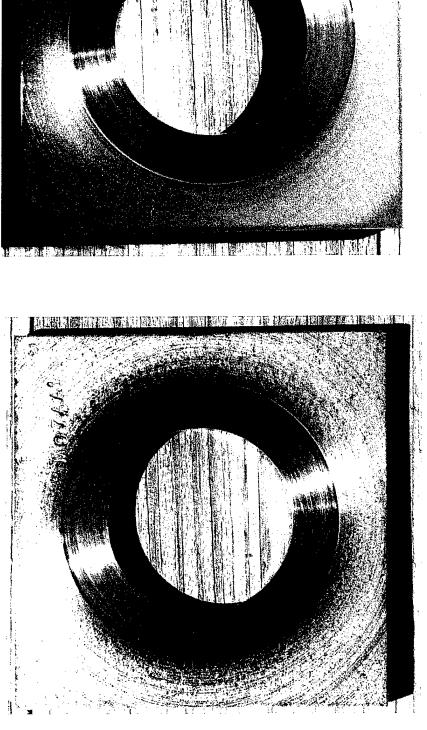


Alloy 718

Alloy 925

Alloy C2000

Figure 22. Wrought Alloys 718, 925, and C2000 After 180 Days in 6 ft/sec (1.8 m/sec) Flowing Natural Seawater





Haynes 25

Figure 23. Cobalt Alloys After 180 Days in 6 ft/sec (1.8 m/sec) Flowing Natural Seawater

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- 4. Kain, R.M., Materials Performance, Vol. 37, No. 8, 1998, p. 62.

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